FTIR studies on the effect of concentration of polyethylene glycol on polimerization of Shellac

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Abstract In the present paper, it was reported the FTIR studies on the efect of polyethylene glycol on polimerization of shellac. The shellac was shellac waxfree, and the solvent was ethanol 96 %. The shellac films were were prepared by solvent-evaporation method. The concentrations of polyethylene glycol having molecular weight of 400 were 10, 30, 60, and 90 w/w %. Three peak intensity bands of C= O stretching of ester at 1709 cm-1, O-H stretching of hydroxyl group at 3400 cm-1, and C-H stretching vibration at 2942 cm^{-1} were observed and related to polimerization of shellac. It was found that polymerization of shellac was slowed down by polyethyelene glycol, and the degree of polymerization of shellac decreased with increasing the concentration of polyethyelene glycol.

1. Introduction

Shellac is a natural polymer derived from resinous secretion of lac insects found in tropical countries, India and Thailand are major users and exporters of shellac [1]. In recent years, competition from Indonesia as a major shellac cultivating country has emerged [2]. Shellac has been utilised in many areas such as; food, medicine, military, electric appliances, printing ink, leather, plastic, metallurgy, machinery and wood varnishes [3]. Shellac has several natural characteristic advantages for use as packaging material or edible coatings, but also some disadvantages. The disadvantage of shellac is its stability, over time its molecular groups can undergo intra-molecular chemical bonding (polymerisation) which leads to changes in its properties, it becomes more brittle and less soluble. Adding plasticizer into natural polymer was one of the effective method to improve the properties of it. Plasticizer is a relatively low molecular weight molecules that can change the physical properties of polymers (e.g. flexibility) and make them more useful as a film-coating material [4]. The mechanistic action of plasticizers is by interposing themselves between individual polymer strands thus breaking down polymer-

polymer interactions. Its easier for the polymer strands to move past each other and become more pliable. PEG has been used as plasticizer for polymers such as PVOH, starch and shellac. It is non-toxic and used in pharmaceuticals compositions and as a food additive, it is thus suitable for food.applications [5]. The composisition, size and shape of a plasticzer and also its compatibility with polymer could affect the interaction between plasticizer and polymer, including its ability to atrract water [6]. The impact of plasticizers on a polymer system were gennerallay affected by factors such as small size, high polarity, more polar group per molecul, and greater distance betwen polar group within a molecule. In our previous studies, it was found that Polyethylene glycol (PEG) could improve stability of shellac. In the present work, it is reported the effect of concentration of PEG on polymerization of shellac. It was argued that the selection of a plasticizer for a spesific system was normally based on the compatibility and permanence of the plasticizer, the amount of necessity of plasticization, and the desired physical properties of the system [7].

2. Experiments

2.1 Materials

Shellac wax free was supplied by Sigma Aldrich UK. Alcohol 96 % was supplied by Merck Germany. Plasticizer polyethylene glycol was supplied by Sigma Aldrich UK.

2.2. Preparation of shellac and plasticised shellac films

All films presented were prepared by solution-casting. Shellac films were made by dissolving 1.25 gr of shellac in 12.5 ml ethanol (96%), while PEG/shellac films (10 wt%) were prepared by mixing and stirring shellac solution and PEG solution. The shellac solutions were made by dissolving 1.125 gr of shellac in 10 ml ethanol and stirred for 2 hours while PEG solutions were made by dissolving 0.125 gr of PEG in 2.5 ml ethanol and stirred for 2 hours using a magnetic bar/stirrer at room temperature.The solution was then cast into Petri dish, then dried at 50 °C for 7 hours before being analysed.

2.3. Characterization using Fourier Transform Infra Red (FTIR)

A Thermo Nicolet NEXUS spectrometer along with a MCT (mercury cadmium telluride) detector cooled by liquid nitrogen was used for all the FTIR analysis. The spectrometer was coupled with a single reflection diamond ATR cell (GrasebySpecac, U.K). This setup has the trade name "Golden Gate". The film was placed on top of the crystal diamond and the spectra of the films taken. The wavelength of interest ranges from 700 to 4000 cm^{-1} and was collected with resolution of 4 cm^{-1} and 64 scans. Omnic software was used to collect and analyse the spectra.

3. Results and Discusssions

The peak intensity of bands of PEG is assiged as O-H stretching of hyroxyl group at 3400 cm-1, C-H stretching of Alkanes at 2900 cm-1, C-H scissor and bending at 1450-1292 cm-1, C-O stretching of Alcohol at 1250 cm-1, and C-O-C at 1100-1060 of ether. The FTIR spectrum of the PEG shellac (10 wt%) system (Figure 1) was the superimposition of spectral patterns of PEG and shellac.

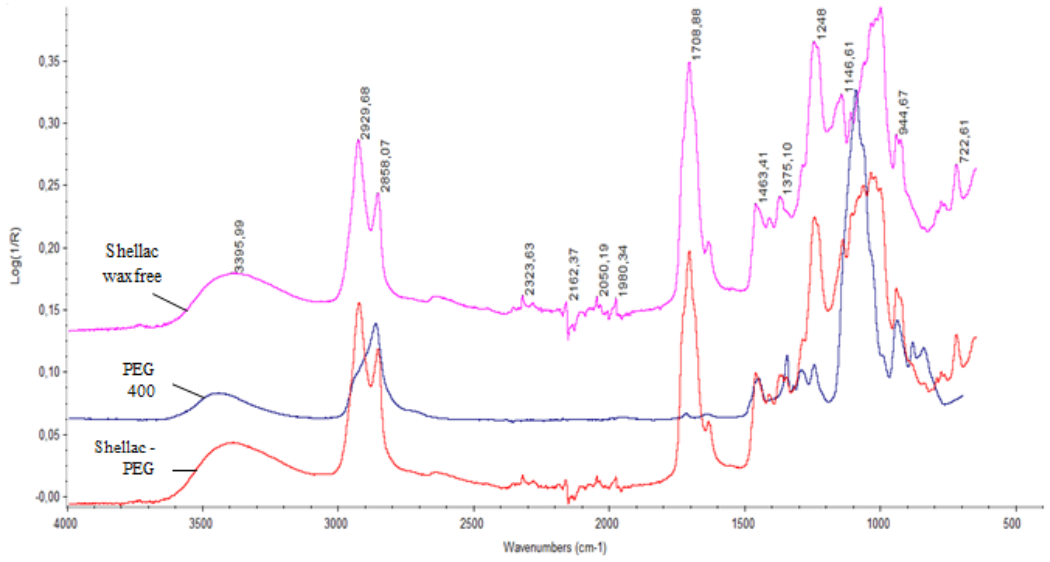

Figure 1. FTIR spectra of shellac, PEG400, and PEG400/shellac system

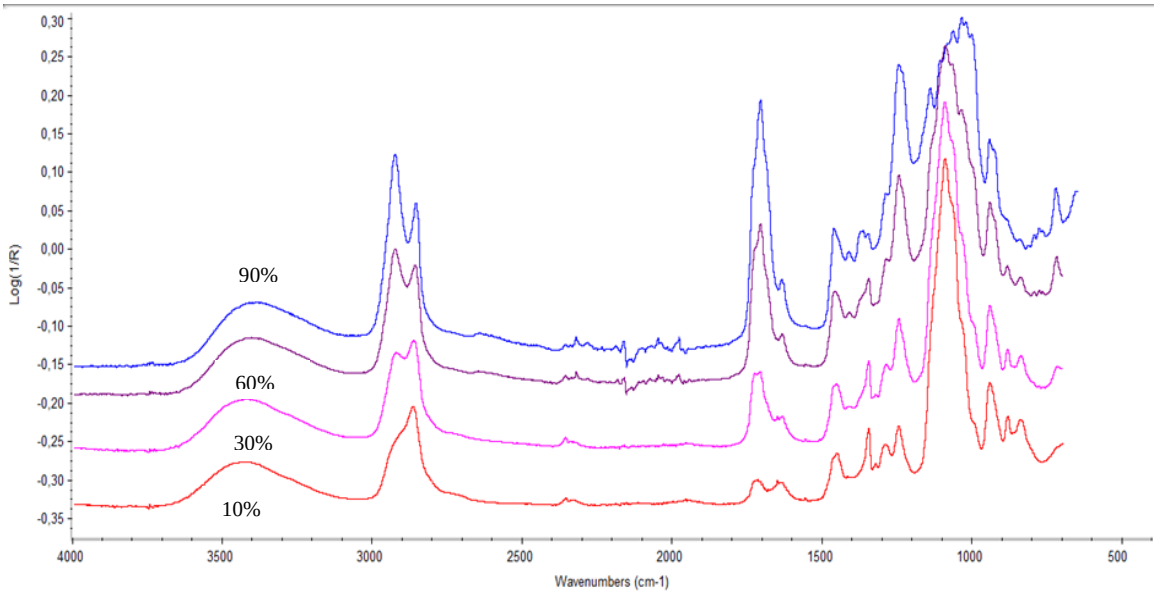

Figure 2. FTIR spectra of PEG400 shellac system with different concentration of PEG400

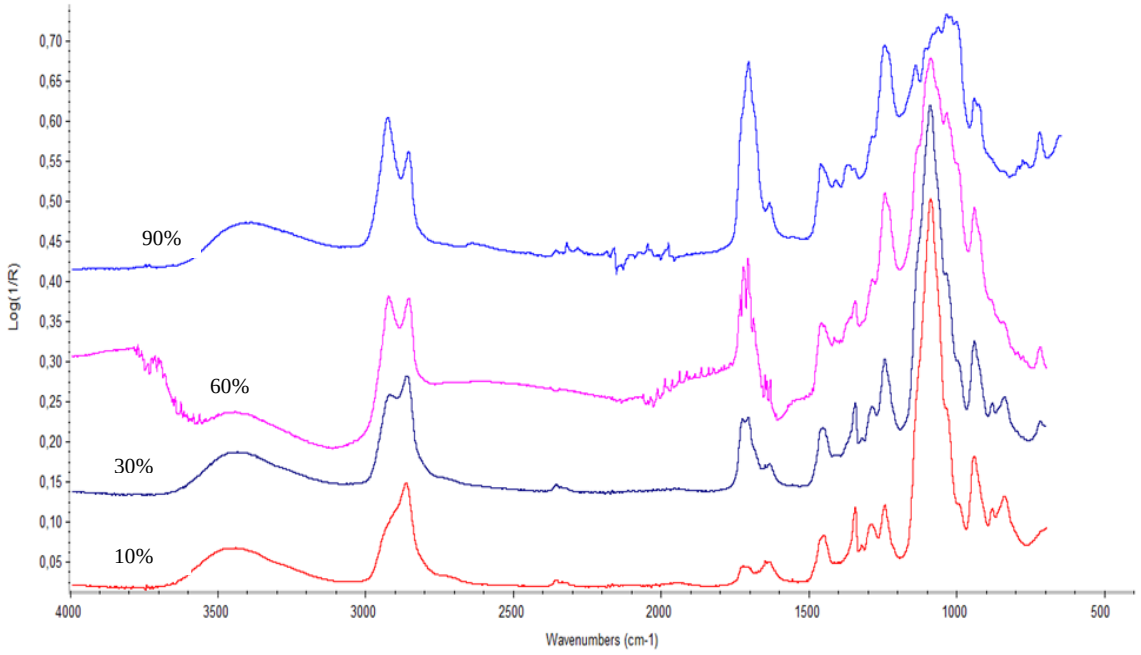

Figure 3. FTIR spectra of PEG400 shellac system with different concentration of PEG400 heated at 125 ^{o}C for 30 minutes

FTIR spectrum of PEG400 shellac system with different concentration (i.e, 10, 30, 60, and 90 wt%) with no heating treatment is shown Figure 2, while the FTIR spectrum of PEG400 shellac system when heating at 125 ^{o}C for 30 minutes is shown in Figure 3 . Peak intensity of O-H, C=O, and C-H of Figure 2 and Figure 3 are shown in Figure 4. It shows that increasing PEG concentration from 10%, to 90% resulted in the increase of peak intensity of O-H grop in PEG shellac system from 0.052, to 0.0754 (no heat in Figure 4a), but decreasing the peak intensity of C=O rom 0.15 to 0.05 (no heat in Figure 4b), while the peak intensity of C-H tended to be constant (no heat in Figure 4c).

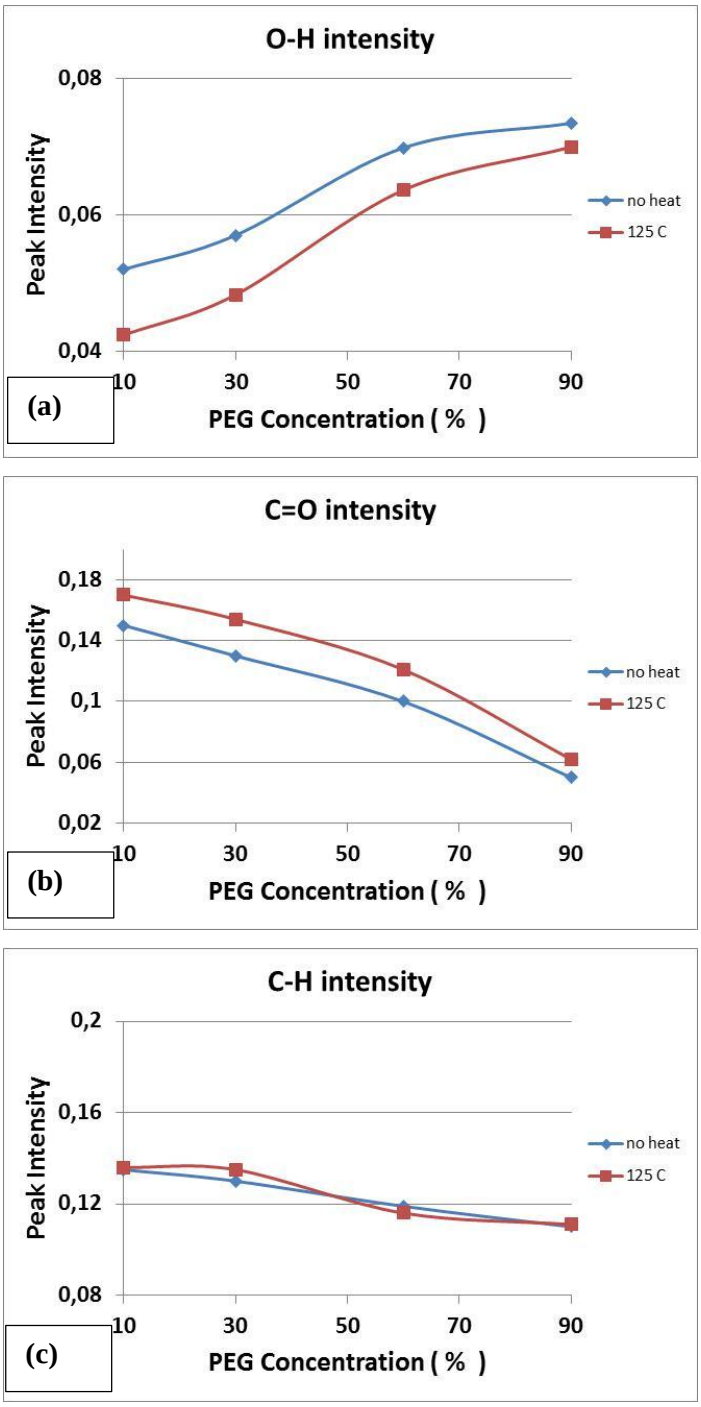

Figure 4. Peak intensity of FTIR spectra of PEG400 shellac system of (a). O-H group, (b). C=O, and (c). C-H group.

One of the main disadvantage of shellac is stability. Over time its molecular groups can undergo intra-molecular chemical bonding called polymerization leading to changes in its properties, it becomes more brittle and less soluble. The polymerization occurs by either heating or exposure to humidity [8]. It is a result of selfesterification of the material [9]. The mechanism of it was proposed by Limmatpavirat [10]. Hence, the stability of shellac can be measured by investigating the hydroxyl and carboxyl group [10,11], and is thus assigned by the increase of peak intensity

bands of C= O stretching of ester at 1709 cm-1, and the decrease of as O-H stretching of hydroxyl group at 3400 cm-1. The intensity of the band at 2942 cm^{-1} occurs due to the C-H stretching vibration [12] and does not change with change in degree of shellac polymerization. The intensity ratios of the band of O-H cm^{-1} to C-H, and the intensity ratios of the band of C=O to C-H from all films then correlates to the polymerization in shellac.

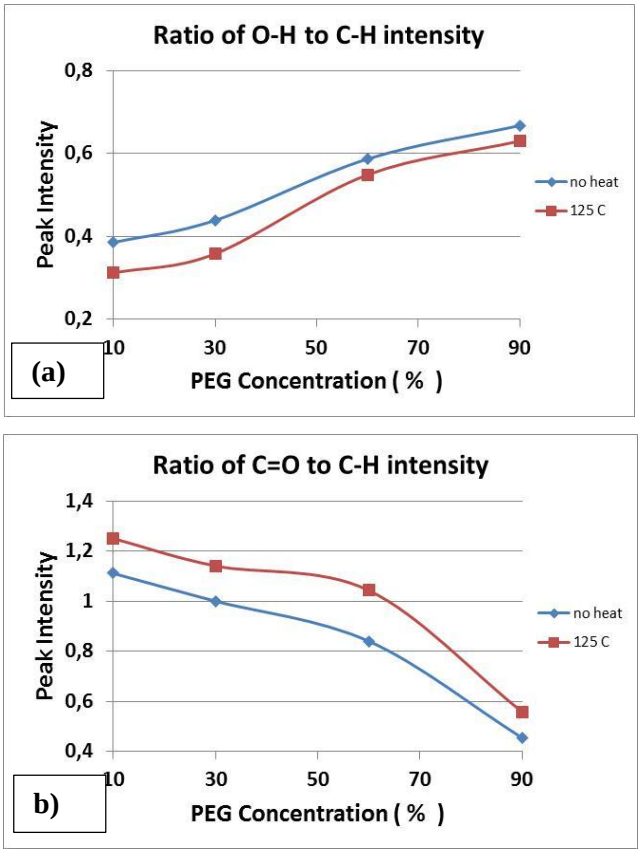

Figure 5. Ratio of peak intensity of FTIR spectra of (a). O-H to C-H (b). C=O, and (b). C=O to C-H

When samples were heated, the energy will break the carboxyl bond to create ester. The peak intensity of O-H, C=O, and C-H of PEG shellac systems heated at 125 ^{o}C for 30 minutes is shown in Figure 4, and the ratio of O-H to C-H and C=O to C-H is shown in Figure 5. It shows siilar trend with PEG shellac system with no heating. Heating samples also resulted in the decrease of O-H group but increasing C=O group, while no change in C-H group. These indicates that introduction of PEG into shellac could not stop polymerization, but slow down polymerization, and the effect of it is higher at high concentration than that of low PEG concentration. Further investigation shows that the slow down of polymerization increases with increasing PEG concentration. The amount of carboxyl group that can be protected by PEG may be higher at high concentration than that of low concentration.

4. Conclusion

FTIR stuides showed that polymerization in shellac was assigned by the decrease of peak intensity ratios of O-H to C-H, and the increase of peak intensity ratio of C=O to C-H. The polymerization was slowed down by PEG, and the degree of polymerization of shellac decreased with increasing the concentration of PEG..

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